Inorg. Chem. **1994**, *33*, 833–836

Isolation and X-ray Crystal Structure of a New Octamolybdate: $[(RhCp^*)_2(\mu_2\text{-}SCH_3)_3]_4[Mo_8O_{26}]\cdot 2CH_3CN$ (Cp^* = $\eta^5\text{-}C_5Me_5$)

Rimo Xi,[†] Bateer Wang,[†,§] Kiyoshi Isobe,[*,†] Takanori Nishioka,[†] Koshiro Toriumi,[‡] and Yoshiki Ozawa[‡]

Institute for Molecular Science, Department of Structural
Molecular Science, The Graduate University for Advanced
Studies, Myodaiji, Okazaki 444 Japan, and Department of
Material Science, Himeji Institute of Technology, Harima
Science Park City, Hyogo 678-12, Japan

Received February 19, 1993

One of the interesting aspects of octamolybdates, $[Mo_8O_{26}]^{4-}$, is seen in varied structural patterns in the solid state and in their structural flexibility in solution. The α-[1] and β-isomers[2] of octamolybdates have been crystallographically confirmed in several salts, and recently the γ-isomer also has been found in $[(CH_3)_3N(CH_2)_6N(CH_3)_3]_2[Mo_8O_{26}]\cdot 2H_2O$.[3] These three isomers are structurally disparate: the α-isomer has approximate D_{3d} symmetry and consists of a ring made up of six MoO_6 octahedra linked to one MoO_4 tetrahedron above and another below its octahedral cavity (α in Figurel); the β-isomer has approximate C_{2h} symmetry and has eight edge-sharing MoO_6 octahedra (β in Figure 1); the γ-isomer has C_i symmetry and is composed of six MoO_6 octahedra interlinked along edges and two MoO_5 trigonal bipyramids each sharing two edges with the octahedra (γ in Figure 1). In acetonitrile, the α-$[Mo_8O_{26}]^{4-}$ anion undergoes intermolecular or intramolecular reorientation of the MoO_4 tetrahedra.[1b] Addition of a small counterion such as K^+ to such the solution induces isomerization to the β-$[Mo_8O_{26}]^{4-}$ anion, for which a "bond-making/breaking" mechanism involving $\alpha \rightleftharpoons \alpha\text{–}\gamma \rightleftharpoons \gamma \rightleftharpoons \beta\text{–}\gamma \rightleftharpoons \beta$ octamolybdate interconversions has been proposed as shown in Figure 1.[4] An alternative "concerted translation" mechanism has been suggested on the basis of ^{95}Mo NMR measurements.[5] We report here the isolation of a new octamolybdate salt of $[(RhCp^*)_2(\mu_2\text{-}SCH_3)_3]_4[Mo_8O_{26}]\cdot 2CH_3CN$ and the results of its crystallographic analysis, which show that it has an approximate α–γ or β–γ intermediate structure.

Results and Discussion

Isolation of the New Octamolybdate. In previous studies, we observed that methanol in the presence of *p*-hydroquinone partly breaks the triple fused cubic framework of $[(RhCp^*)_4Mo_4O_{16}]$[6] to give an incomplete double cubane-type cluster $[(RhCp^*)_2Mo_3O_9(OCH_3)_4]$.[7] On the other hand, we have found that methanethiol induces a reconstruction of the cluster framework separating the organometallic and oxide parts with formation of the new octamolybdate salt of $[(RhCp^*)_2(\mu_2\text{-}SCH_3)_3]_4[Mo_8O_{26}]$.

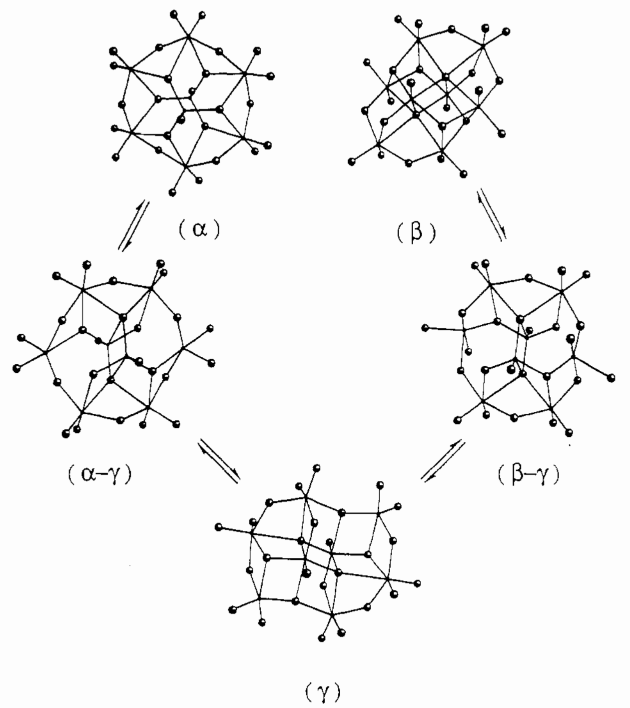

Figure 1. Structures of the α-, β-, γ-, α–γ-, and β–γ-$[Mo_8O_{26}]^{4-}$ isomers in the proposed mechanism for the α-β isomerization in ref 4a. The α, β, and γ structures are depicted by using X-ray analytical results shown in refs 1c, 2h, and 3, respectively. The α–γ and β–γ structures are taken from ref 4a. Small circles represent molybdenums and large circles represent oxygens.

A mixture of $[(RhCp^*)_4Mo_4O_{16}]\cdot 2H_2O$ and CH_3SH in CH_3OH was refluxed under an Ar atmosphere for 3.5 h to yield a yellow precipitate.[8] When an acetonitrile solution of the product was allowed to stand for 3 days, orange crystals of $[(RhCp^*)_2(\mu_2\text{-}SCH_3)_3]_4[Mo_8O_{26}]\cdot 2CH_3CN$ were obtained in a 23% yield. The formation of the octamolybdate proceeds according to eq 1.

$$2[(RhCp^*)_4Mo_4O_{16}]\cdot 2H_2O + 12CH_3SH \rightarrow [(RhCp^*)_2(\mu_2\text{-}SCH_3)_3]_4[Mo_8O_{26}] + 8H_2O \quad (1)$$

Structure of $[(RhCp^*)_2(\mu_2\text{-}SCH_3)_3]_4[Mo_8O_{26}]\cdot 2CH_3CN$. The X-ray crystal structure of the salt was determined, and the ORTEP diagram and the polyhedral model of the anionic part are shown in parts A and B, respectively, of Figure 2. The salt is made up of an octamolybdate unit, four cations of $[(RhCp^*)_2(\mu_2\text{-}SCH_3)_3]^+$, and two acetonitrile molecules of crystallization. The anion has approximate C_{2h} symmetry and consists of a Mo_6O_6 ring capped on opposite faces by tripodal MoO_4 tetrahedra. The characteristic feature of this structure is that the Mo_6O_6 ring contains two tetrahedrally and four octahedrally coordinated Mo(VI) atoms; thus, its framework is distorted from the D_{3d} symmetry of the α-isomer[1] and elongated along a C_2 axis through two tetrahedrally coordinated Mo atoms in the Mo_6O_6 ring. In the ring, the linkage

---

[†] Institute for Molecular Science.

[‡] Himeji Institute of Technology.

[§] Present Address: Institute of Coordination Chemistry, Inner Mongolia Normal University, Huhhot, Inner Mongolia 010022, China.

(1) (a) Fuchs, J.; Hartl, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 375. (b) Day, V. W.; Fredrich, M. F.; Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1977**, *99*, 952. (c) Hsieh, T.-C.; Shaikh, S. N.; Zubieta, J. *Inorg. Chem.* **1987**, *26*, 4079.

(2) (a) Lindqvist, I. *Ark. Kemi* **1950**, *2*, 349. (b) Atovmyan, L. O.; Krasochka, O. N. *Zh. Strukt. Khim.* **1972**, *13*, 342. (c) Gatehouse, B. M. *J. Less-Common Met.* **1977**, *54*, 283. (d) Vivier, H.; Bernard, J.; Djomaa, H. *Rev. Chim. Miner.* **1977**, *14*, 584. (e) Roman, P.; Jaud, J.; Galy, J. *Z. Kristallogr.* **1981**, *154*, 59. (f) Weakley, T. J. R. *Polyhedron* **1982**, *1*, 17. (g) Hountas, A.; Filippakis, S. E. *Cryst. Struct. Commun.* **1982**, *11*, 1087. (h) Kroenke, W. J.; Fackler, J. P., Jr.; Mazany, A. M. *Inorg. Chem.* **1983**, *22*, 2412. (i) Piggott, B.; Wong, S. F.; Hursthouse, M. B.; Short, R. L. *Polyhedron* **1988**, *7*, 2605. (j) Fitzroy, M. D.; Fallon, G. D.; Murray, K. S. *Inorg. Chim. Acta* **1989**, *157*, 187.

(3) Niven, M. L.; Cruywagen, J. J.; Heyns, J. B. B. *J. Chem. Soc., Dalton Trans.* **1991**, 2007.

(4) (a) Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1976**, *98*, 8291. (b) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Inorganic Chemistry Concepts No. 8; Springer-Verlag: Berlin, Heidelberg, Germany, New York, Tokyo, 1983; pp 138–140.

(5) Masters, A. F.; Gheller, S. F.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *Inorg. Chem.* **1980**, *19*, 3866.

(6) Hayashi, Y.; Toriumi, K.; Isobe, K. *J. Am. Chem. Soc.* **1988**, *110*, 3666.

(7) Do, Y.; You, X.-Z.; Zhang, C.; Ozawa, Y.; Isobe, K. *J. Am. Chem. Soc.* **1991**, *113*, 5892.

(8) The reaction performed under other conditions gave different products, linear type tetranuclear complexes, $[\{(RhCp^*)(\mu_2\text{-}SCH_3)_3Mo(O)_2\}_2(\mu_2\text{-}O)]$, $[\{(RhCp^*)(\mu_2\text{-}SCH_3)_3Mo(O)\}_2(\mu_2\text{-}O)_2]$, and $[\{(RhCp^*)(\mu_2\text{-}SCH_3)_3Mo(O)\}_2(\mu_2\text{-}S)(\mu_2\text{-}O)]$. These compounds will be reported elsewhere.

0020-1669/94/1333-0833$04.50/0

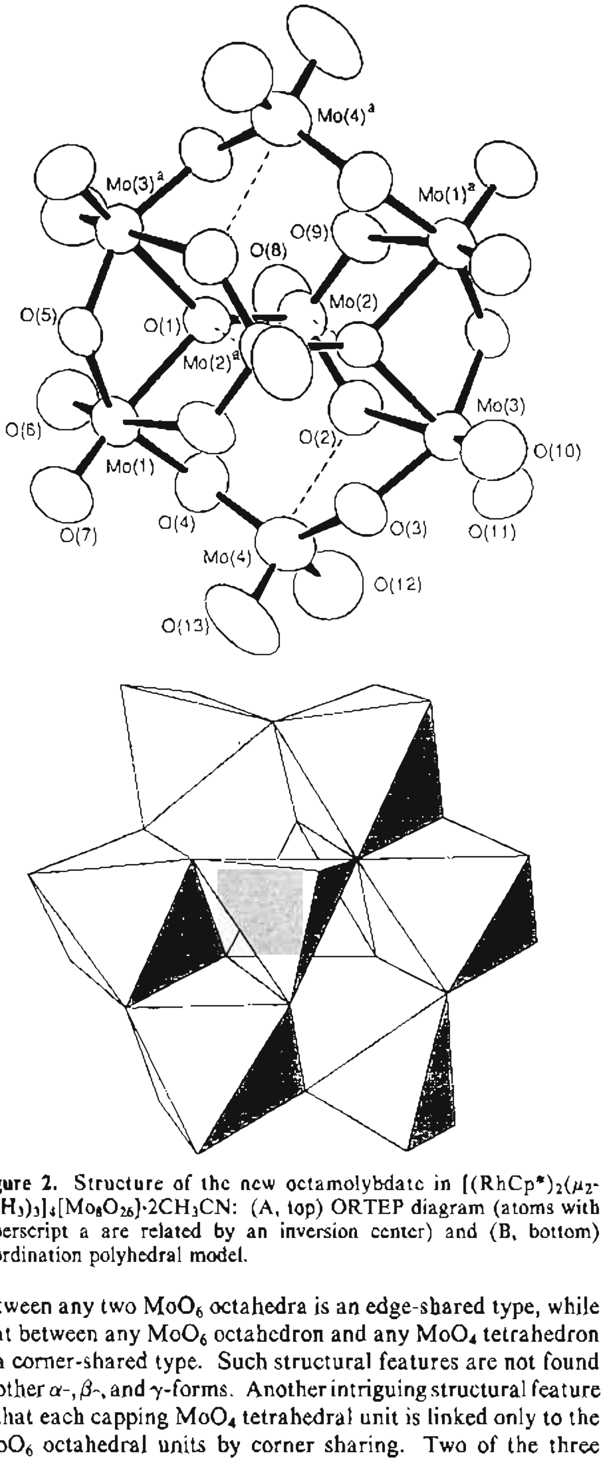

Figure 2. Structure of the new octamolybdate in $[(RhCp^*)_2(\mu_2\text{-}SCH_3)_3]_4[Mo_8O_{26}]\cdot 2CH_3CN$: (A, top) ORTEP diagram (atoms with superscript a are related by an inversion center) and (B, bottom) coordination polyhedral model.

Table 1. Crystallographic Data and Structure Refinement Parameters for $[(RhCp^*)_2(\mu\text{-}SMe)_3]_4[Mo_8O_{26}]\cdot 2CH_3CN$

formula: $C_{96}H_{162}Mo_8N_2O_{26}Rh_8S_{12}$
$a = 15.595(4)$ Å
$b = 17.284(4)$ Å
$c = 15.284(4)$ Å
$\alpha = 99.33(1)°$
$\beta = 117.81(1)°$
$\gamma = 106.68(1)°$
$V = 3222(2)$ Å^3
$Z = 1$

fw = 3735.82
space group = $P\bar{1}$ (No. 2)
$T = 25$ °C
$\lambda = 0.710\,73$ Å
$\rho_{calcd} = 1.925$ g cm^{-3}
$\mu = 19.586$ cm^{-1}
$R^a = 0.055$
$R_w{}^b = 0.065$

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o - F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w^{-1} = [\sigma^2(F_o) + (0.020F_o)^2]$.

between any two MoO_6 octahedra is an edge-shared type, while that between any MoO_6 octahedron and any MoO_4 tetrahedron is a corner-shared type. Such structural features are not found in other α-, β-, and γ-forms. Another intriguing structural feature is that each capping MoO_4 tetrahedral unit is linked only to the MoO_6 octahedral units by corner sharing. Two of the three bridging oxygen atoms used in the tetrahedral unit are of the μ_2-O type (O(2) and O(9)) and the other is of the μ_3-O type (O(1)). Each capping MoO_4 tetrahedron in the α-isomer is linked by a differnt corner sharing arrangement to all six MoO_6 octahedra in the ring through three μ_3-O atoms. The β- and γ-isomers, of course, do not have any capping tetrahedron as shown in Figure 1. The structure of the $[Mo_8O_{26}]^{4-}$ anion, as determined here, is hence different from those of α-, β- (including other β-forms modified by coordination of organic bases[9]), and γ-isomers. Selected bond distances and angles of the new octamolybdate are shown in Table 3. Each MoO_6 octahedron (Mo(1) and Mo(3)) is distorted, and has two short cis-, two medium trans-, and two long cis-Mo–O bonds in the range of 1.690–1.706 Å for short, 1.911–1.960 Å for medium, and 2.308–2.350 Å for long bonds. The MoO_4 tetrahedra in the ring each have two short (1.677 and 1.70 Å) and two medium Mo–O bonds (1.829 and 1.833 Å). All molybdenum atoms in the ring have two terminal Mo–O(t) bonds in the short range, indicating double bond character. The capping MoO_4 units have three kinds of Mo–O bonds; Mo–O(t) (1.698 Å), Mo–O(μ_2) (1.780 and 1.760 Å), and Mo–O(μ_3) (1.836 Å). For this cluster, we see the expected trend of Mo–O distance increasing in direct proportion with an increasing coordination number of oxygens (i.e., one < two < three).[3] Both ring and capping MoO_4 tetrahedral units have O–Mo–O angles in the ranges of 107.4–111.6 and 108.2–123.1°, respectively, showing a deviation from that of a regular tetrahedron. Each Mo atom in these MoO_4 units has another adjacent oxygen atom: Mo(4) in the ring is situated at the position of 2.730 Å from O(2), and Mo(2) in the cap is at a distance of 2.878 Å from O(1)^a (as indicated by the broken lines in Figure 2A). If these distances were to be shortened slightly until a bonding character develops, all MoO_4 tetrahedra would then be converted to five-coordinate MoO_5 units, and the resulting octamolybdate would have a structure identical to that of the α–γ- or β–γ-isomer.[10] These compounds have been proposed by Klemperer and Shum as intermediates in their study of interconversion of isomeric α- and β-forms (Figure 1). This means that the structure of the new octamolybdate approximates that of the α–γ or β–γ intermediate. This would further suggest that an approximate α–γ or β–γ conformation is at an energy minimum. Finding of the new octamolybdate as well as the γ-form in $[(CH_3)_3N(CH_2)_6N(CH_3)_3]_2[Mo_8O_{26}]\cdot 2H_2O$[3] suggests a "bond-making/breaking" mechanism[4] for the facile isomerization of the α- and β-forms. Kinetic and mechanistic studies will be needed, however, to differentiate between the two possible mechanisms.[5]

In the crystal structure of the new octamolybdate salt, two of the four cationic $[(RhCp^*)_2(\mu_2\text{-}SCH_3)_3]^+$ counterions are crystallographically independent and have no bonding interaction with the $[Mo_8O_{26}]^{4-}$ anion. Three SCH_3 ligands bridge the two $RhCp^*$ groups, wherein the two Cp^* ligands in an eclipse conformation coordinate to the Rh atoms perpendicularly to the Rh···Rh axis, as found in the previously synthesized compound, $[(RhCp^*)_2(\mu_2\text{-}SCH_3)_3]_2[W_3S_9]$.[11] The bonding distances and angles of the cationic parts (supplementary material) are also quite similar to those in the tungsten–trimer salt. The acetonitriles of crystallization, which are symmetry related, are located such that they have no interaction with the anion and the cation.

IR Spectra of the New Octamolybdate in the Solid State and in Nitromethane. The new octamolybdate is soluble enough in nitromethane to measure the IR spectra in the range 1000–700 cm^{-1}. The compounds, $[(n\text{-}C_4H_9)_4N]_4[Mo_8O_{26}]$ and $[(n\text{-}C_4H_9)_4N]_3K[Mo_8O_{26}]\cdot 2H_2O$, were also subjected to an IR study in nitromethane to compare their IR data with those of the new octamolybdate, although these two compounds have already been

---

(9) (a) McCarron, III, E. M.; Whitney, J. F.; Chase, D. B. *Inorg. Chem.* **1984**, *23*, 3275. (b) Gili, P.; Martín-Zarza, P.; Martín-Reyes, G.; Arrieta, J. M.; Madariaga, G. *Polyhedron*, **1992**, *11*, 115. (c) Martín-Zarza, P.; Arrieta, J. M.; Muñoz-Roca, M. C.; Gili, P. *J. Chem. Soc., Dalton Trans.* 1993, 1551.

(10) These two isomers are constitutionally identical, differing only in configuration at five-coordinate MoO_5 units in the ring (see ref 4a).

(11) Hou, Z.; Ozawa, Y.; Isobe, K. *Chem. Lett.* **1990**, 1863.

Table 2. Atomic Parameters for $[(RhCp^*)_2(\mu\text{-}SMe)_3]_4[Mo_8O_{26}]\cdot 2CH_3CN$: Fractional Coordinates and Equivalent Isotropic Thermal Parameters ($Å^2$)

	x/a	y/b	z/c	U_{eq}[c]		x/a	y/b	z/c	U_{eq}[c]
Rh(1)	0.59699(4)	0.65908(3)	0.31232(4)	0.0240(2)	C(18)	0.4136(6)	0.6243(6)	0.0652(6)	0.048(4)
Rh(2)	0.84521(4)	0.70362(3)	0.40460(4)	0.0253(2)	C(19)	0.3993(7)	0.4626(5)	0.1529(7)	0.054(4)
Rh(3)	0.44885(4)	0.81344(3)	0.79204(4)	0.0255(2)	C(20)	0.4539(7)	0.5387(6)	0.3850(7)	0.048(5)
Rh(4)	0.70066(4)	0.87494(3)	0.88492(4)	0.0325(3)	C(21)	0.9593(5)	0.6587(4)	0.3935(5)	0.029(3)
Mo(1)	1.16600(4)	0.60023(4)	0.25496(4)	0.0305(3)	C(22)	0.9817(5)	0.6755(4)	0.4998(5)	0.030(3)
Mo(2)	0.88821(4)	0.51120(3)	0.00278(4)	0.0282(2)	C(23)	1.0070(5)	0.7653(5)	0.5431(6)	0.039(4)
Mo(3)	0.85736(4)	0.28889(3)	−0.09408(4)	0.0318(3)	C(24)	1.0015(5)	0.8041(5)	0.4677(7)	0.040(4)
Mo(4)	1.01018(6)	0.37458(5)	0.17444(5)	0.0529(4)	C(25)	0.9732(5)	0.7390(5)	0.3748(6)	0.035(4)
S(1)[a]	0.7020(2)	0.5774(1)	0.3710(2)	0.019(1)	C(26)	0.9314(6)	0.5728(5)	0.3194(7)	0.043(4)
S(2)[a]	0.7057(2)	0.6967(2)	0.2432(2)	0.026(1)	C(27)	0.9827(6)	0.6067(5)	0.5519(7)	0.042(4)
S(3)[a]	0.7581(2)	0.7681(2)	0.4658(2)	0.029(1)	C(28)	1.0375(7)	0.8091(6)	0.6548(7)	0.064(5)
S(4)[a]	0.5961(2)	0.9508(1)	0.8877(2)	0.024(1)	C(29)	1.0350(8)	0.9002(6)	0.486(1)	0.073(7)
S(5)[a]	0.5449(2)	0.8000(1)	0.7102(2)	0.022(1)	C(30)	0.9640(7)	0.7544(7)	0.2780(8)	0.060(6)
S(6)[a]	0.5821(2)	0.7759(2)	0.9146(2)	0.026(1)	C(31)	0.2858(5)	0.7201(5)	0.6688(5)	0.034(3)
S(11)[b]	0.6857(6)	0.5896(5)	0.2641(7)	0.070(4)	C(32)	0.3050(5)	0.7187(5)	0.7681(6)	0.034(3)
S(12)[b]	0.7390(7)	0.7816(6)	0.3354(9)	0.082(6)	C(33)	0.3290(6)	0.8016(5)	0.8309(6)	0.039(4)
S(13)[b]	0.7381(6)	0.6720(6)	0.4774(6)	0.066(4)	C(34)	0.3236(5)	0.8558(5)	0.7644(7)	0.044(4)
S(14)[b]	0.6042(6)	0.9020(5)	0.9644(5)	0.053(4)	C(35)	0.2989(5)	0.8053(5)	0.6686(6)	0.039(4)
S(15)[b]	0.5651(6)	0.8975(5)	0.7475(6)	0.052(4)	C(36)	0.2525(7)	0.6437(7)	0.5774(7)	0.067(5)
S(16)[b]	0.5589(6)	0.7375(4)	0.8101(6)	0.056(4)	C(37)	0.2980(7)	0.6399(5)	0.8033(7)	0.054(5)
O(1)	1.0306(3)	0.5846(3)	0.0881(4)	0.032(2)	C(38)	0.3390(8)	0.8257(6)	0.9360(8)	0.065(6)
O(2)	0.8630(4)	0.4054(3)	0.0131(4)	0.037(3)	C(39)	0.3379(8)	0.9497(6)	0.802(1)	0.071(7)
O(3)	0.9826(4)	0.3171(3)	0.0456(4)	0.038(2)	C(40)	0.2806(8)	0.8325(8)	0.5716(9)	0.077(7)
O(4)	1.0534(4)	0.4929(3)	0.2261(4)	0.037(3)	C(41)	0.8402(6)	0.8457(6)	0.9541(9)	0.061(5)
O(5)	1.2306(3)	0.6769(3)	0.2035(3)	0.029(2)	C(42)	0.8605(6)	0.9252(6)	1.0254(8)	0.059(5)
O(6)	1.1379(4)	0.6711(3)	0.3175(4)	0.043(3)	C(43)	0.8567(7)	0.9861(7)	0.979(1)	0.077(6)
O(7)	1.2732(4)	0.5952(4)	0.3540(4)	0.043(3)	C(44)	0.8312(7)	0.9556(7)	0.878(1)	0.070(6)
O(8)	0.8216(4)	0.5539(4)	0.0435(4)	0.047(3)	C(45)	0.8217(7)	0.8628(9)	0.8588(8)	0.085(6)
O(9)	0.8381(4)	0.5035(3)	−0.1296(4)	0.037(3)	C(46)	0.8444(8)	0.7665(8)	0.982(1)	0.12(1)
O(10)	0.8897(5)	0.2247(3)	−0.1604(5)	0.049(3)	C(47)	0.890(1)	0.930(1)	1.136(1)	0.13(1)
O(11)	0.7614(4)	0.2169(3)	−0.0868(5)	0.048(3)	C(48)	0.880(1)	1.0791(8)	1.036(2)	0.14(1)
O(12)	0.9079(6)	0.3248(5)	0.1876(5)	0.082(5)	C(49)	0.826(1)	1.010(1)	0.807(1)	0.12(1)
O(13)	1.1118(7)	0.3571(5)	0.2621(5)	0.099(5)	C(50)	0.806(1)	0.802(1)	0.763(1)	0.14(1)
N	0.635(1)	0.9819(8)	0.508(1)	0.14(1)	C(51)	0.7228(7)	0.5711(7)	0.4948(7)	0.059(5)
C(11)	0.4829(5)	0.6831(5)	0.3456(6)	0.031(4)	C(52)	0.6679(7)	0.5987(8)	0.1395(7)	0.070(5)
C(12)	0.4736(5)	0.7074(4)	0.2570(6)	0.028(3)	C(53)	0.7737(8)	0.8717(6)	0.441(1)	0.087(8)
C(13)	0.4423(5)	0.6303(5)	0.1760(6)	0.032(3)	C(54)	0.5834(7)	1.0101(5)	0.7957(8)	0.055(5)
C(14)	0.4349(5)	0.5600(4)	0.2127(6)	0.030(3)	C(55)	0.5252(7)	0.6851(5)	0.6784(8)	0.056(5)
C(15)	0.4587(5)	0.5919(4)	0.3194(6)	0.031(3)	C(56)	0.6135(8)	0.8282(7)	1.0466(7)	0.063(6)
C(16)	0.5121(7)	0.7432(5)	0.4469(7)	0.047(5)	C(57)	0.6467(8)	1.0469(6)	0.5592(8)	0.064(6)
C(17)	0.4825(6)	0.7950(5)	0.2454(7)	0.042(4)	C(58)	0.662(1)	1.1266(7)	0.623(1)	0.087(7)

[a] Occupancies of the atoms are fixed at 0.667 in the course of refinement. [b] Occupancies of the atoms are fixed at 0.333 in the course of refinement. [c] $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j \mathbf{a}_i\cdot\mathbf{a}_j$.

studied in acetonitrile.[4a] IR specta of these three compounds in the Mo–O(t) and Mo–O(b) (b = bridging) stretching regions are shown in Figure 3 (a, α-form; b, β-form; and c, the new octamolybdate, for the solid and d, α-form; e, β-form; and f, the new octamolybdate, for a nitromethane solution). Spectral patterns of the three compounds in the solid state are different from one another. For the new octamolybdate, the Mo–O stretching band of 801 cm^{-1} is particularly characteristic (Figure 3c). The new octamolybdate in nitromethane gives the spectrum shown in Figure 3f, which is also different from that of the solid state and is presumed to be partly comprised of a combination of the spectra of $[(n\text{-}C_4H_9)_4N]_4[Mo_8O_{26}]$ and $[(n\text{-}C_4H_9)_4N]_3K[Mo_8O_{26}]\cdot 2H_2O$. These two compounds (although pure α- and β-isomers, respectively, in the solid state), consist of α–β mixtures in nitromethane (Figure 3d,e) as in acetonitrile.[4a] Although further careful experiments are needed to elucidate the $\alpha \rightleftharpoons \beta$ equilibrium via several intermediates, we may stabilize these intermediates by using appropriate solvents and countercations. Large countercations particularly seem to be important in isolating intermediary octamolybdates containing four-[12] and five-coordinate Mo(VI) units.[3]

Experimental Section

Reagents and Solvents. The following chemicals were purchased from commercial sources and used without further purification: $RhCl_3\cdot 3H_2O$ (Shiga Kikinzoku); pentamethylcyclopentadiene (Kanto Kagaku); $Na_2MoO_4\cdot 2H_2O$ (Wako); $[(n\text{-}C_4H_9)_4N]Cl$ (Wako); 30% CH_3SH methanol solution (Nakalai); CD_3NO_2 (Aldrich). Methanol and acetonitrile were distilled under Ar. $[RhCp^*Cl_2]_2$[13] and $[(RhCp^*)_4Mo_4O_{16}]\cdot 2H_2O$[6] were prepared according to the procedure described earlier. $[(n\text{-}C_4H_9)_4N]_4[Mo_8O_{26}]$ and $[(n\text{-}C_4H_9)_4N]_3K[Mo_8O_{26}]\cdot 2H_2O$ were synthesized according to Klemperer's method.[4a]

Analytical Procedures. Elemental analyses were performed by the IMS Chemical Material Center. IR spectra were measured in KBr pellets and in nitromethane with NaCl cell (path length, 0.025 mm) on a Perkin-Elmer 1600 Series FTIR spectrometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL GX 400 NMR spectrometer in CD_3NO_2. X-ray structural analysis of an orange single crystal of the new octamolybdate was performed as follows. The intensity data were collected on an Enraf-Nonius CAD4 diffractometer with Mo Kα radiation (λ = 0.710 37 Å) in the $2° < 2\theta < 50°$ range at 298 K. The intensities for reflection were corrected for Lorentz–polarization factors and an absorption effect (numerical Gaussian integration method), but not for extinction. The minimum and maximum transmission coefficients were 0.718 and 0.556, respectively. The cell dimensions were determined by least-squares fitting of 25 centered reflections ($20° < 2\theta < 25°$). Crystallographic data are listed in Table 1, and fractional coordinates are listed in Table 2. In the crystal structure analysis, the positions of rhodium and molybdenum atoms were determined by direct methods, and other non-hydrogen atoms were located on the Fourier map. Six sulfur atoms in two $(Cp^*Rh)_2(SCH_3)_3$ groups are disordered at two possible sites. The occupancies of each site were determined by simultaneous refinement of the thermal parameters and occupancies, and fixed at 0.667 and 0.333 respectively,

---

[12] Day, V. W.; Fredrich, M. F.; Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1977**, *99*, 6146.

[13] Hayashi, Y.; Ozawa, Y.; Isobe, K. *Inorg. Chem.* **1991**, *30*, 1025.

Table 3. Bond Distances (Å) and Angles (deg) in $[(RhCp^*)_2(\mu_2\text{-}SCH_3)_3]_4[Mo_8O_{26}]\cdot 2CH_3CN$

Mo(1)–O(1)	2.338(4)	Mo(1)–O(4)	1.946(5)
Mo(1)–O(5)	1.911(6)	Mo(1)–O(6)	1.697(7)
Mo(1)–O(7)	1.690(5)	Mo(1)–O(9)^a	2.350(6)
Mo(2)–O(1)	1.836(4)	Mo(2)–O(2)	1.780(6)
Mo(2)–O(8)	1.698(8)	Mo(2)–O(9)	1.760(6)
Mo(3)–O(1)^a	2.308(5)	Mo(3)–O(2)	2.310(6)
Mo(3)–O(3)	1.960(4)	Mo(3)–O(5)^a	1.912(5)
Mo(3)–O(10)	1.706(8)	Mo(3)–O(11)	1.704(7)
Mo(4)–O(3)	1.833(6)	Mo(4)–O(4)	1.829(5)
Mo(4)–O(12)	1.70(1)	Mo(4)–O(13)	1.677(9)
Mo(2)–Mo(1)–Mo(3)^a	64.94(2)	Mo(2)–Mo(1)–Mo(4)	65.11(2)
Mo(3)^a–Mo(1)–Mo(4)	124.48(2)	Mo(2)–Mo(1)–Mo(2)^a	58.32(2)
Mo(4)–Mo(1)–Mo(2)^a	71.27(2)	Mo(3)^a–Mo(1)–Mo(1)^a	62.88(3)
O(1)–Mo(1)–O(4)	80.1(2)	O(1)–Mo(1)–O(5)	72.7(2)
O(1)–Mo(1)–O(6)	92.5(2)	O(1)–Mo(1)–O(7)	163.2(3)
O(1)–Mo(1)–O(9)	72.6(2)	O(4)–Mo(1)–O(5)	149.2(2)
O(4)–Mo(1)–O(6)	97.2(3)	O(4)–Mo(1)–O(7)	100.3(3)
O(4)–Mo(1)–O(9)	77.6(2)	O(5)–Mo(1)–O(6)	98.2(3)
O(5)–Mo(1)–O(7)	101.6(3)	O(5)–Mo(1)–O(9)	80.6(2)
O(6)–Mo(1)–O(7)	104.1(3)	O(6)–Mo(1)–O(9)	164.8(2)
O(7)–Mo(1)–O(9)	90.9(3)		
Mo(1)–Mo(2)–Mo(3)^a	50.68(2)	Mo(1)–Mo(2)–Mo(4)	53.84(2)
Mo(1)–Mo(2)–Mo(1)^a	121.68(3)	Mo(1)–Mo(2)–Mo(2)^a	58.46(3)
Mo(1)–Mo(2)–Mo(3)	98.36(2)	Mo(1)–Mo(2)–Mo(4)^a	95.93(3)
Mo(3)^a–Mo(2)–Mo(4)	101.07(3)	Mo(3)^a–Mo(2)–Mo(1)^a	97.66(3)
Mo(3)^a–Mo(2)–Mo(2)^a	57.92(2)	Mo(3)^a–Mo(2)–Mo(3)	121.68(3)
Mo(3)^a–Mo(2)–Mo(4)^a	49.86(2)	Mo(4)–Mo(2)–Mo(1)^a	102.75(3)
Mo(4)–Mo(2)–Mo(2)^a	66.56(2)	Mo(4)–Mo(2)–Mo(3)	52.93(2)
Mo(4)–Mo(2)–Mo(4)^a	126.93(3)	Mo(1)^a–Mo(2)–Mo(2)^a	63.21(2)
Mo(1)^a–Mo(2)–Mo(3)	53.58(2)	Mo(1)^a–Mo(2)–Mo(4)^a	53.00(2)
Mo(2)^a–Mo(2)–Mo(3)	63.76(2)	Mo(2)^a–Mo(2)–Mo(4)^a	60.37(2)
Mo(3)–Mo(2)–Mo(4)^a	100.71(3)		
O(1)–Mo(2)–O(2)	111.6(2)	O(1)–Mo(2)–O(8)	108.1(2)
O(1)–Mo(2)–O(9)	111.1(3)	O(2)–Mo(2)–O(8)	107.4(3)
O(2)–Mo(2)–O(9)	110.4(2)	O(8)–Mo(2)–O(9)	107.9(3)
Mo(1)–Mo(3)–Mo(2)	64.37(2)	Mo(1)–Mo(3)–Mo(2)^a	63.55(2)
Mo(1)–Mo(3)–Mo(4)^a	126.06(3)	Mo(2)–Mo(3)–Mo(2)^a	58.32(2)
Mo(2)–Mo(3)–Mo(4)^a	70.31(2)	Mo(2)^a–Mo(3)–Mo(4)^a	68.59(2)
O(1)^a–Mo(3)–O(3)	82.2(2)	O1^a–Mo(3)–O(5)^a	73.4(2)
O(1)^a–Mo(3)–O(10)	92.3(3)	O(1)^a–Mo(3)–O(11)	162.7(3)
O(1)^a–Mo(3)–O(2)	72.7(2)	O(3)–Mo(3)–O(5)^a	151.4(2)
O(3)–Mo(3)–O(10)	94.8(3)	O(3)–Mo(3)–O(11)	99.9(3)
O(3)–Mo(3)–O(2)	75.9(2)	O(5)^a–Mo(3)–O(10)	100.7(3)
O(5)^a–Mo(3)–O(11)	99.2(3)	O(5)^a–Mo(3)–O(2)	82.7(2)
O(10)–Mo(3)–O(11)	104.6(3)	O(10)–Mo(3)–O(2)	163.1(2)
O(11)–Mo(3)–O(2)	91.0(3)		
Mo(1)–Mo(4)–Mo(2)	61.05(3)	Mo(1)–Mo(4)–Mo(2)^a	55.73(2)
Mo(1)–Mo(4)–Mo(3)	109.08(3)	Mo(2)–Mo(4)–Mo(2)^a	53.07(2)
Mo(2)–Mo(4)–Mo(3)	58.47(2)	Mo(2)^a–Mo(4)–Mo(3)	59.83(3)
O(4)–Mo(4)–O(12)	108.2(4)	O(4)–Mo(4)–O(13)	103.9(3)
O(4)–Mo(4)–O(3)	123.1(3)	O(12)–Mo(4)–O(13)	104.5(5)
O(12)–Mo(4)–O(3)	110.6(3)	O(13)–Mo(4)–O(3)	104.7(4)

[a] Symmetry code: $2 - x, 1 - y, z$.

for final refinement. Atomic scattering factors and anomalous dispersions were taken from ref 14. All non-hydrogen atoms were found and refined by full-matrix refinement techniques using Xtal 3.0 program. The final R and R_w values were 0.050 and 0.065 for 735 variables and 10 707 independent reflections with $F > 3.0\sigma(F)$.

Preparation of $[(RhCp^*)_2(\mu_2\text{-}SCH_3)_3]_4[Mo_8O_{26}]\cdot 2CH_3CN$. A mixture of $[(RhCp^*)_4Mo_4O_{16}]\cdot 2H_2O$ (2.0 g, 1.2 mmol) and CH_3SH (22.8 mmol: 4.5 cm^3 of 30% methanol solution) in methanol (15 cm^3) was refluxed under an Ar atmosphere with stirring for 3.5 h. After the mixture was refluxed, the resulting yellow crystalline solid was isolated by filtration. When an acetonitrile solution of the product was allowed to stand for 3 days, orange crystals of $[(RhCp^*)_2(\mu_2\text{-}SCH_3)_3]_4[Mo_8O_{26}]\cdot 2CH_3CN$ were obtained in a 23% yield (0.53 g). ^{1}H NMR (CD_3NO_2, 22 °C): C_5Me_5 δ 1.820(s), SCH_3 δ 1.979 (t, J_{Rh-H} = 1.2 Hz). ^{13}C NMR (CD_3NO_2, 22 °C): C_5Me_5 δ 9.411(s), SCH_3 δ 13.555(s), C_5Me_5 δ 99.120 (d, J_{Rh-C} = 6.1 Hz). IR (KBr disk): Mo–O stretching region, 942 (s), 911 (s), 861 (w), 844 (w), 801 (w), 712 (s) cm^{-1}. IR (CH_3NO_2 solution): Mo–O stretching region, 965 (vw), 944 (m), 925 (m), 911 (s), 858 (m), 832 (w), 810 (m), 778 (m), 736 (w), 717 (m) cm^{-1}. Anal. Calcd for $C_{96}H_{162}Mo_8N_2O_{26}Rh_8S_{12}$: C, 30.86; H, 4.37; N, 0.75. Found: C, 30.75; H, 4.44: N, 0.82.

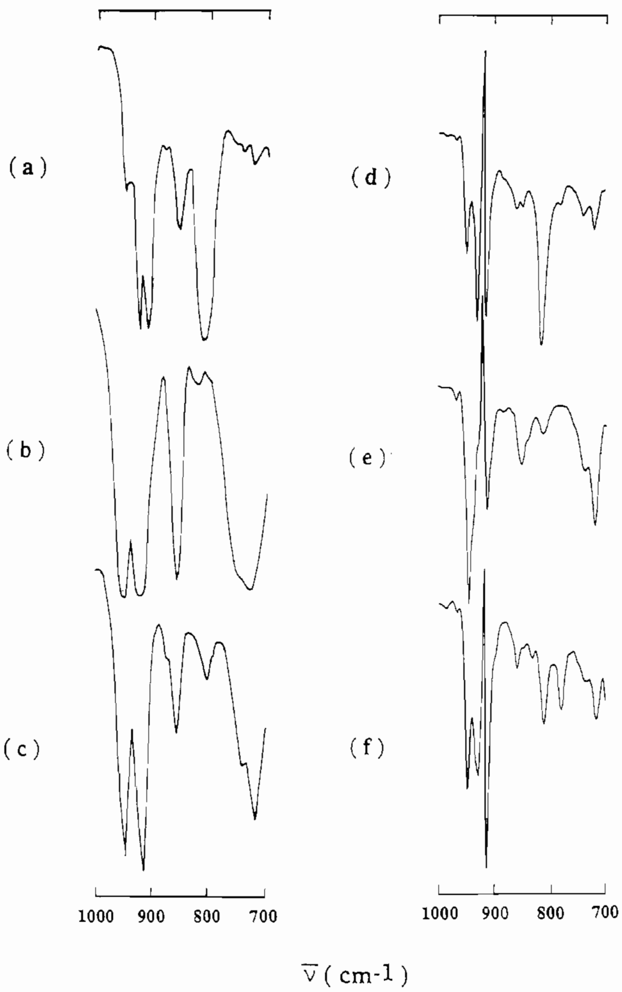

Figure 3. IR spectra of (a) $[(n\text{-}C_4H_9)_4N]_4[Mo_8O_{26}]$ in KBr pellet (b) $[(n\text{-}C_4H_9)_4N]_3K[Mo_8O_{26}]\cdot 2H_2O$ in KBr pellet, (c) the new octamolybdate salt in KBr pellet, (d) $[(n\text{-}C_4H_9)_4N]_4[Mo_8O_{26}]$ in CH_3NO_2, (e) $[(n\text{-}C_4H_9)_4N]_3K[Mo_8O_{26}]\cdot 2H_2O$ in CH_3NO_2, and (f) the new octamolybdate salt in CH_3NO_2.

Acknowledgment. We wish to thank Professor W. G. Klemperer (University of Illinois) for discussion and information of the α–β $[Mo_8O_{26}]^{4-}$ isomerization and IR measurement of these octamolybdates in CH_3CN and the Japanese Ministry of Education, Science and Culture for financial support (Grant-in-Aid for Scientific Research 04640588 and Grant in Aid for Scientific Research on Priority Areas 04241102).

Supplementary Material Available: Figures for the structures of the two unequivalent cations, $[(RhCp^*)_2(\mu_2\text{-}SCH_3)_3]^+$, and tables of anisotropic thermal parameters and bond lengths and angles (10 pages). Ordering information is given on any current masthead page.

---

(14) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.